

## Contract Report

### **High Throughput, Low Toxic Processing of Very Thin, High Efficiency CIGSS Solar Cells**

**NREL contract no. XXL-5-44205-08, UCF/FSEC Account no. 2012 8098**

**Year 3, Quarter 2 Report**

**Report no. FSEC-CR-1733-07**

November 27, 2007

*Prepared for*

National Renewable Energy Laboratory  
1617 Cole Boulevard  
Golden, CO 80401

*Submitted by*

Neelkanth G. Dhere  
Florida Solar Energy Center<sup>®</sup>  
1679 Clearlake Road  
Cocoa, FL 32922-5703



## TABLE OF CONTENTS

TABLE OF CONTENTS.....	2
1. $\text{Si}_x\text{N}_y/\text{Mo}$ DEPOSITION .....	3
2. CIGS2 THIN FILM SOLAR CELLS .....	4
3. ZnCdS AND ZnS AS ALTERNATIVE BUFFER LAYER FOR CIGS2 SOLAR CELLS .....	9
4. REFERENCES .....	12

## 1. Si<sub>x</sub>N<sub>y</sub>/Mo DEPOSITION

Si<sub>x</sub>N<sub>y</sub>/Mo depositions were carried out on glass samples. Si<sub>x</sub>N<sub>y</sub> layer is required as diffusion barrier layer to prevent sodium diffusion from sodalime glass to CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2-y</sub>S<sub>y</sub> (CIGSeS) layer. Si<sub>x</sub>N<sub>y</sub> films were deposited by reactive RF magnetron sputtering from silicon target in the presence of nitrogen. Silicon target was bonded to the target backing plate and allowed the adhesive to cure for >24 hours. Afterwards the silicon target was mounted in place of CuGa target in the CuGa/In/Mo DC magnetron sputtering chamber. The RF tuning network was shifted from ZnO/ZnO:Al bilayer RF magnetron sputtering chamber to sputtering source having newly mounted silicon target. Gas line connection for nitrogen including mass flow controller, and control unit were made.

1" x 4" glass substrates were thoroughly washed and cleaned with ultrasonic cleaning using cold soap solution, warm soap solution, isopropanol, and distilled deionized water. Partial pressures of sputtering gases during the Si<sub>x</sub>N<sub>y</sub> deposition were as follows: argon  $8 \times 10^{-4}$  Torr and nitrogen  $8 \times 10^{-4}$  Torr, the total pressure being  $1.6 \times 10^{-3}$  Torr. Si<sub>x</sub>N<sub>y</sub> deposition was carried out using RF power of 225 watt and the substrate movement duration of 600 seconds per inch was used. Sheet resistance measurement and thickness measurement using surface profilometer were carried out on the Si<sub>x</sub>N<sub>y</sub> films formed. Sheet resistance measurements showed that the Si<sub>x</sub>N<sub>y</sub> films were insulating and the thickness was approximately 750 Å.

Molybdenum was sputter-deposited on Si<sub>x</sub>N<sub>y</sub> layers. Mo being refractory material develops stresses. It is essential to deposit stress-free and relatively inert Mo films in order to achieve well adherent and highly efficient CIGSeS absorber thin film solar cells[1]. Molybdenum when deposited using dc magnetron technique exhibits a correlation between sputtering gas pressure (argon) and developed residual stress. During molybdenum deposition, films deposited at sputtering power of 300 W and  $3 \times 10^{-4}$  Torr argon pressure develop compressive stress; while the films deposited at 200 W and  $5 \times 10^{-3}$  Torr pressure develop tensile stress. It is suggested that such stress reversals are dependent on energetic bombardment by reflected neutrals and/or sputtered atoms. The working gas pressure is expected to moderate the flux and energy of these particles. At relatively low pressures, the arriving atoms have high kinetic energy and the resulting film has dense microstructure, experiencing compressive stress. This compressive stress is explained by atomic peening caused by the impact of energetic particles. At relatively high pressures, less energy is provided to the film because of scattering and the resulting film exhibits an open porous microstructure, as the film is experiencing tensile stress. A well-adherent molybdenum layer reasonably free of residual stress were sputter-deposited using total of 5 Mo layers in which two Mo layers with tensile stress were sandwiched between three Mo layers having compressive stress, alternate layers are used to reduce the overall stress in the Mo films. Three (initial, middle and final) Mo layers with compressive stress were sputtered using high sputtering power and low sputtering gas pressure. The remaining two Mo layers having tensile stress were sputtered using low sputtering power and high sputtering gas pressure. The sputtering parameters for high power/low pressure cycle were 300 watt,  $3 \times 10^{-4}$  Torr and the substrate movement duration of 32 seconds per inch was used for each cycle. And the sputtering parameters for low power/high pressure cycle were 200 watt and  $5 \times 10^{-3}$  Torr and the substrate movement duration of 37.5 seconds per inch was used for each cycle. The sheet resistance measured at various locations of the sputtered molybdenum films was approximately  $0.6 \Omega/\square$ .

Complete fabrication of CIGSeS thin film solar cells is being carried out on these sputtered molybdenum films as well as on commercially available molybdenum coated glass

substrates without the  $\text{Si}_x\text{N}_y$  diffusion barrier layer. Thus CIGSeS cells will be completed under identical conditions on both molybdenum films one having  $\text{Si}_x\text{N}_y$  diffusion barrier layer and the other with no  $\text{Si}_x\text{N}_y$  diffusion barrier layer and detailed analyses will be carried out.

## 2. CIGS2 THIN FILM SOLAR CELLS

Electrical characterization was carried out on a  $1.8 \mu\text{m}$  thick absorber Copper-indium-gallium sulfide (CIGS2) /CdS cell at the Colorado State University. The results are as follows:

### 1) Current-Voltage characteristics:

Figure 1 shows current-voltage characteristics under dark and illuminated conditions. The photovoltaic parameters are as follows: efficiency = 9.4%, FF=63.6%,  $J_{sc}=19.4 \text{ mA/cm}^2$ ,  $V_{oc}=0.76 \text{ V}$ .

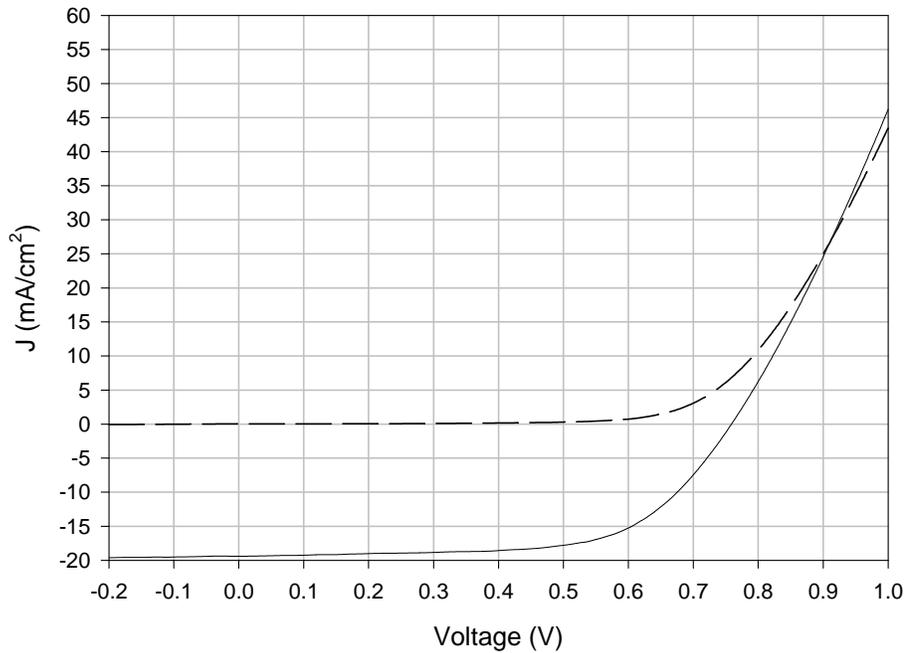


Figure 1: Current-Voltage characteristics of CIGS2/CdS cell.

## 2) Determination of absorber bandgap

Figure 2 shows dependence of the open circuit voltage on temperature. Intercept of the linear extrapolation with the  $V_{oc}(T)$  axis again suggests an absorber band gap value of approximately 1.4 eV.

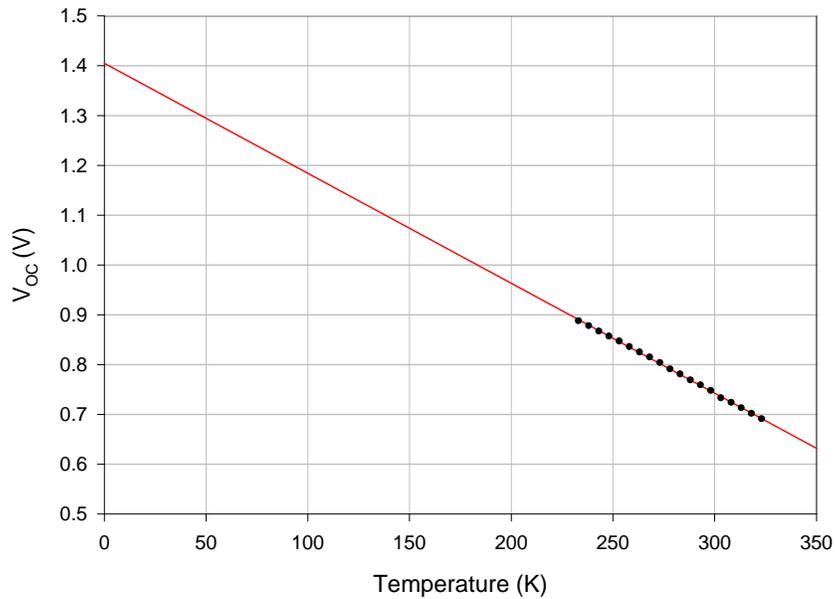


Figure 2: Bandgap determination.

## 3) LBIC measurements:

Results from light beam induced current (LBIC) measurements performed with 638-nm laser at three different resolutions are shown in figures 3, 4 and 5. LBIC map is accompanied with a histogram which gives a slightly more quantitative estimate of device uniformity. One of the devices was scanned at different voltages with low resolution and one feature on that device was also scanned with a medium resolution at four different voltages.

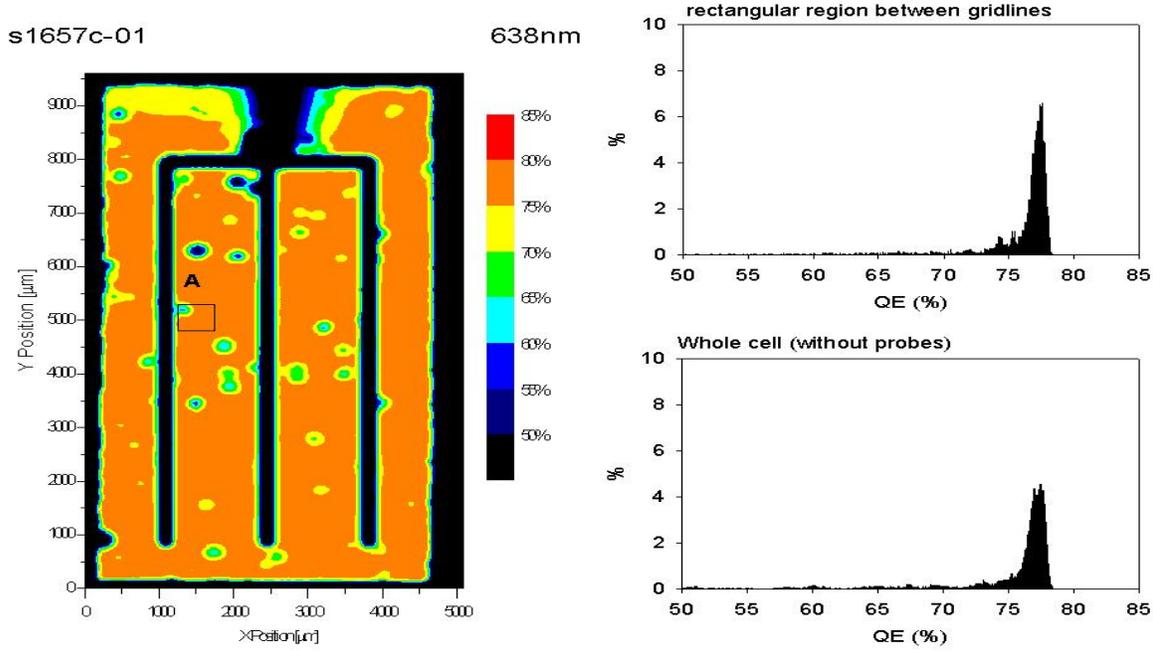
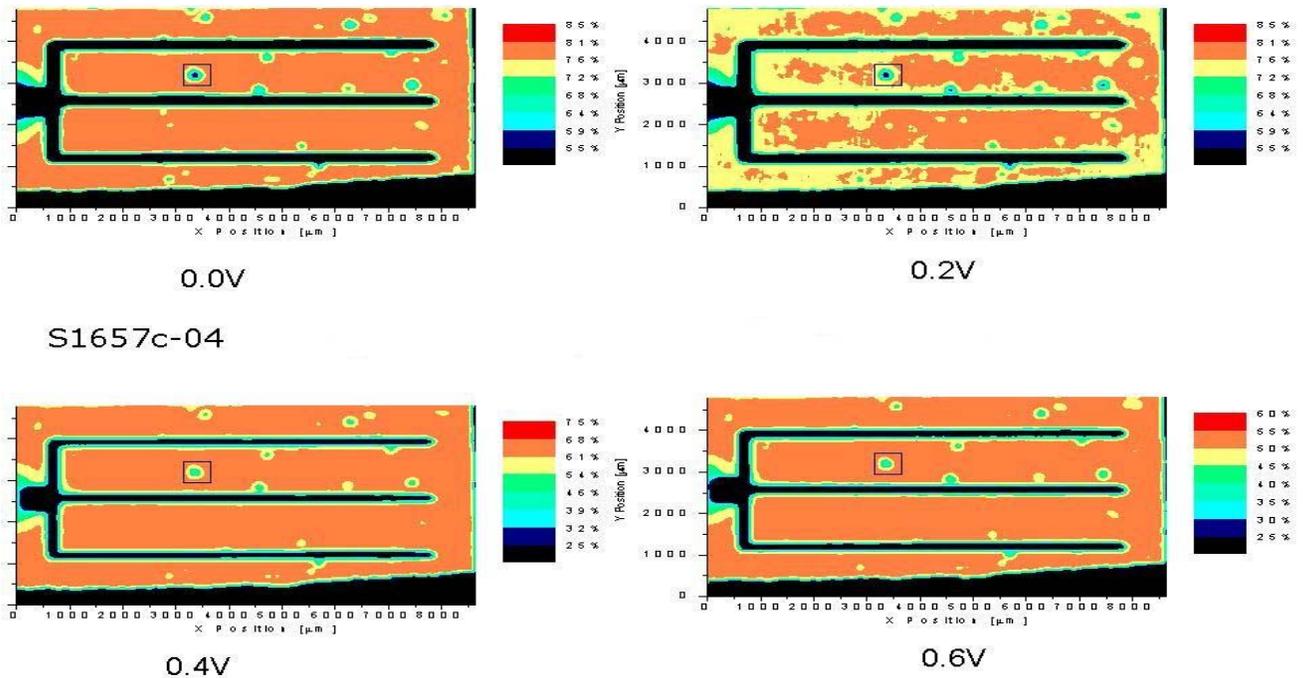


Figure 3: LBIC images



\*scales are different

Figure 4: LBIC at different operating biases

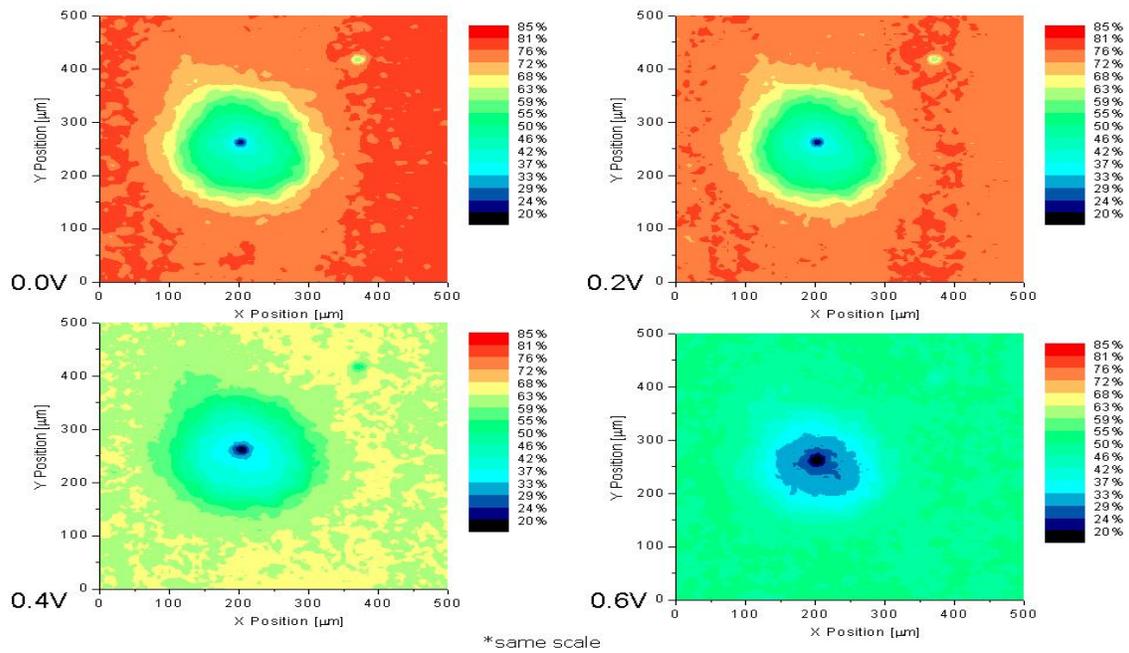


Figure 5: High resolution of the square portion from figure 4.

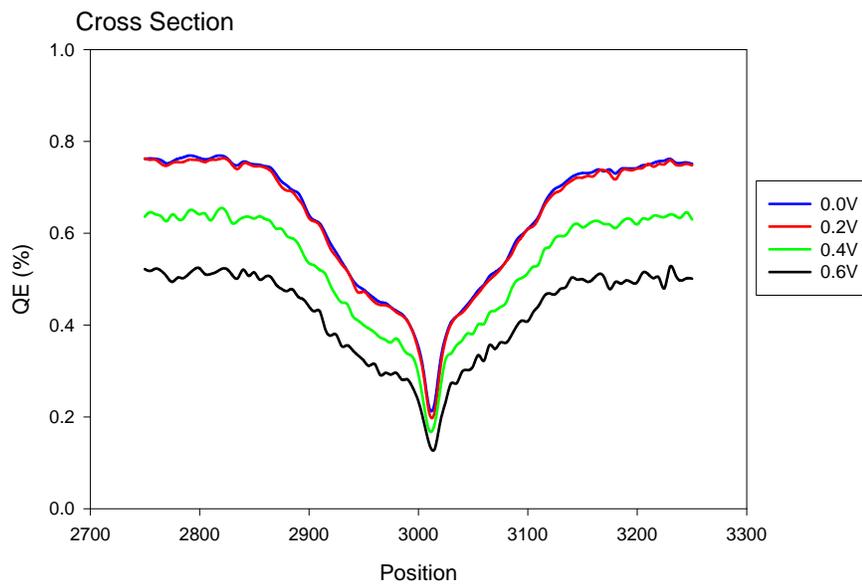


Figure 6: Cross-sections of the features shown in figure 5.

Figure 6 shows cross sections of the features. The shape of the cross section does not change with voltage, which suggests that it is not a local shunt. The fact that all points on the curve shift down by almost the same amount suggests that it might be an optical defect.

### 3. ZnCdS AND ZnS AS ALTERNATIVE BUFFER LAYER FOR CIGS2 SOLAR CELLS

Photovoltaic characterization CIGS2/CdZnS cell having CIGS2 absorber thickness of 1.8  $\mu\text{m}$  was carried out at the Colorado State University. The results are provided in the following:

1) *Current-Voltage characteristics:*

The efficiency obtained was 8.1%. Other parameters were:  $\text{FF}=55.4\%$ ,  $J_{\text{sc}}=18.9\text{mA}/\text{cm}^2$ ,  $V_{\text{oc}}=0.78\text{ V}$ .

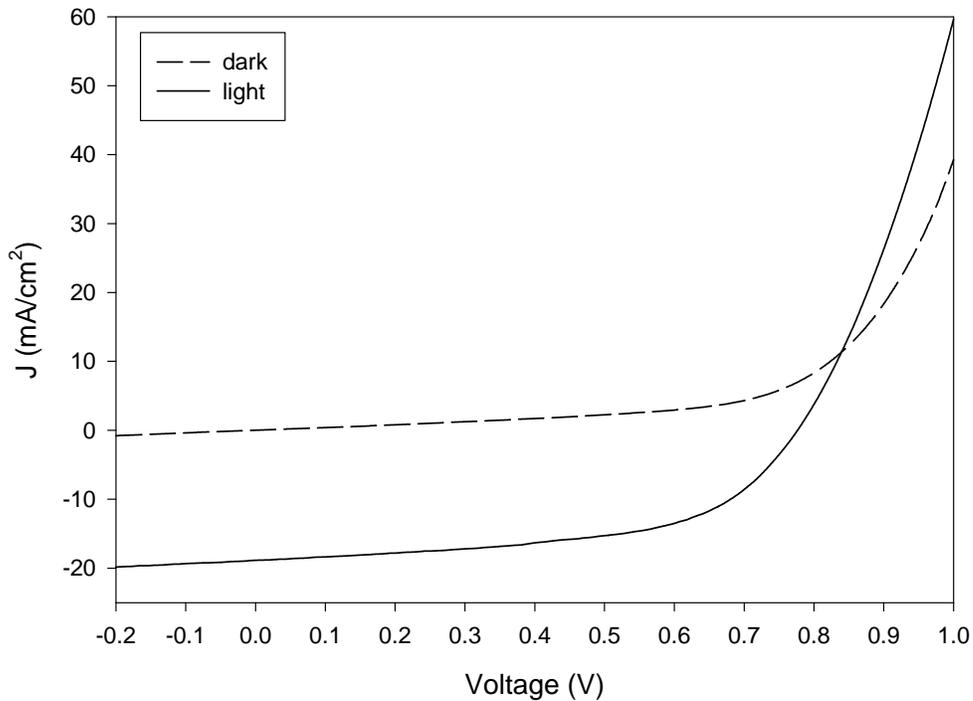


Figure 7: Current-Voltage characteristics of CIGS2/CdZnS cell.

Figure 8 shows experimental I-V curves at different temperatures 233K, 273K and 313K. Figure 8 shows dark and light curves superposition failure, also known as the crossover effect, which is thought to take place due to the presence of the conduction band offset. The conduction band offset is defined as the difference between electron affinities of CIGS2 and CdZnS layers.

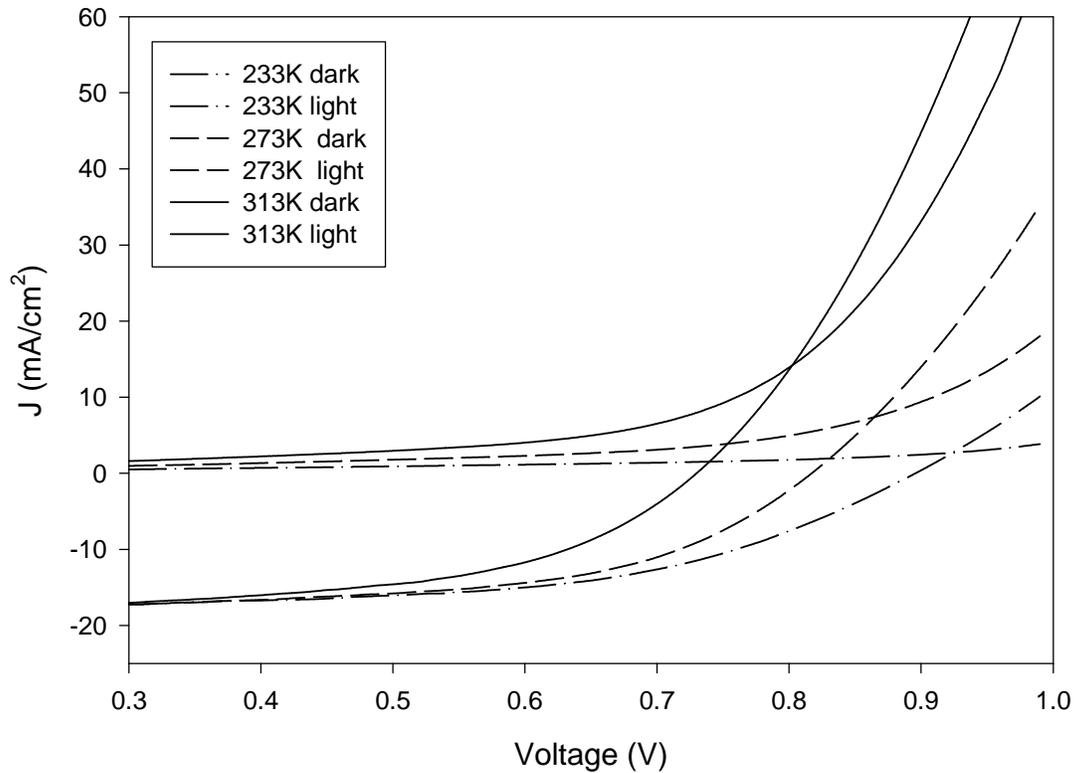


Figure 8: Experimental I-V curves at different temperatures

## 2) LBIC measurements:

Light-beam-induced-current (LBIC) measurements provide a direct link between the spatial non-uniformities inherent in thin-film polycrystalline solar cells, and the overall performance of these cells. Figure 9 shows that CIGS2 solar cell fabricated with  $Zn_xCd_{1-x}S$  as heterojunction partner has uniformity variations of 3%. Limited uniformity variations indicates good quality cell.

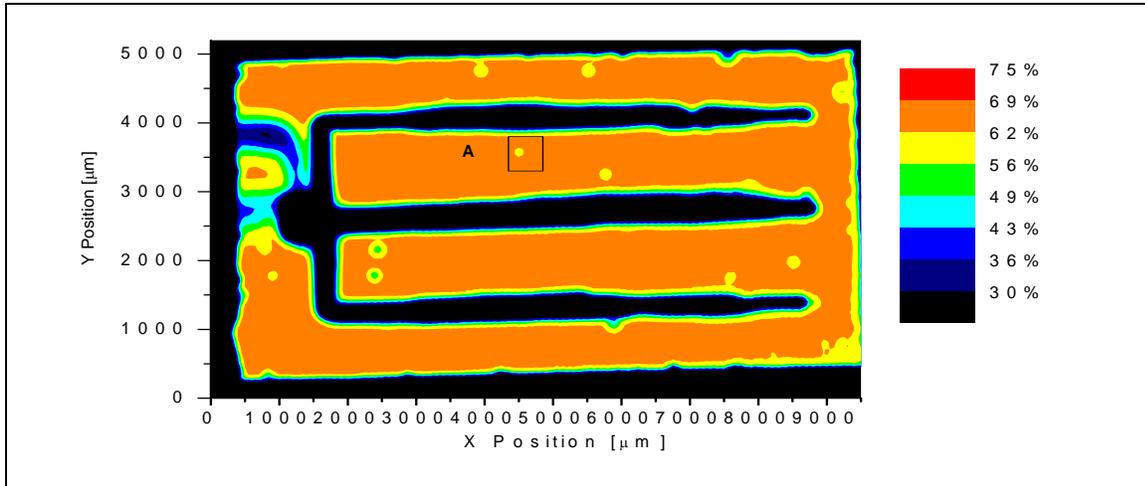


Figure 9: LBIC measurements for SLG/Mo/CIGS2/Zn<sub>x</sub>Cd<sub>1-x</sub>S/i-ZnO/ZnO: Al devices (#1657CZ) performed with 638-nm laser measured at Colorado State University.

**3) Capacitance-Voltage Measurement:**

The Capacitance-Voltage measurement of cell #1657CZ was carried out at Colorado State University. The slope of the linear extrapolation of plot has shown average hole density in the CIGS2 absorber layer of  $1.6 \times 10^{17} \text{ cm}^{-3}$ .

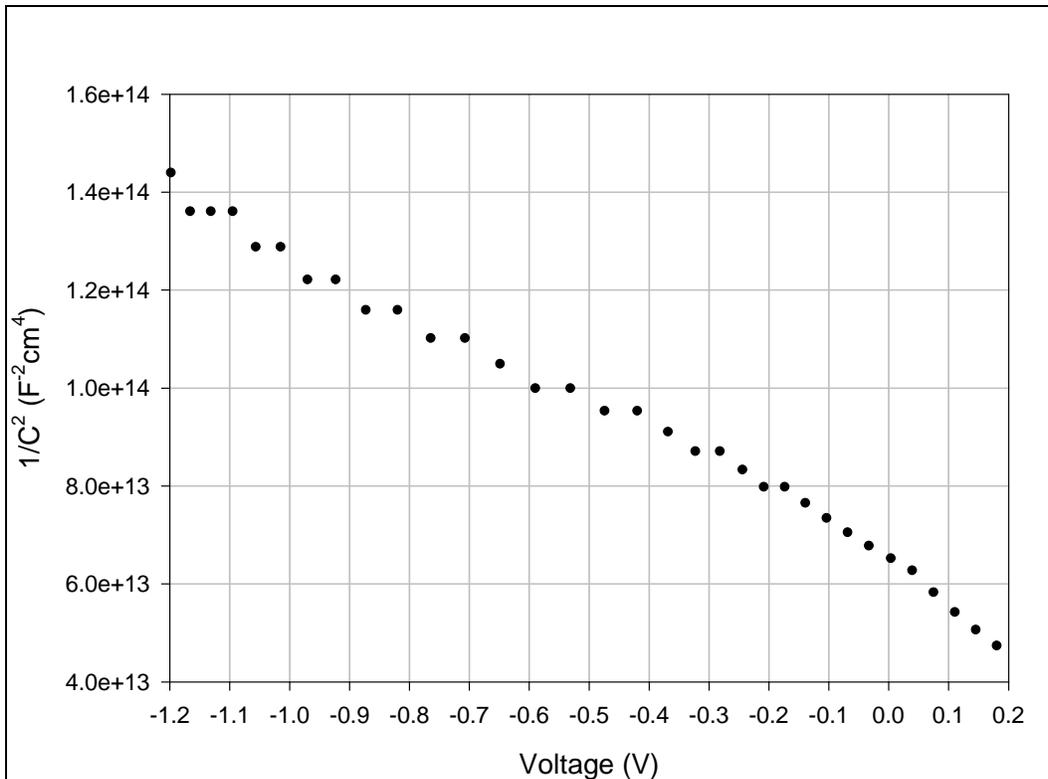


Figure 10: C<sup>-2</sup> dependence on voltage.

#### **4. REFERENCES**

- [1] Ankur A. Kadam, Neelkanth G. Dhere, Paul Holloway, Evan Law, "Study of molybdenum back contact layer to achieve adherent and efficient CIGS2 absorber thin-film solar cells", J. Vac. Sci. Technol. A 23 (4) Jul/Aug 2005 pages 1197-1201.